

The Development of Low Temperature Li-Ion Electrolytes for Past, Present and Future NASA Missions

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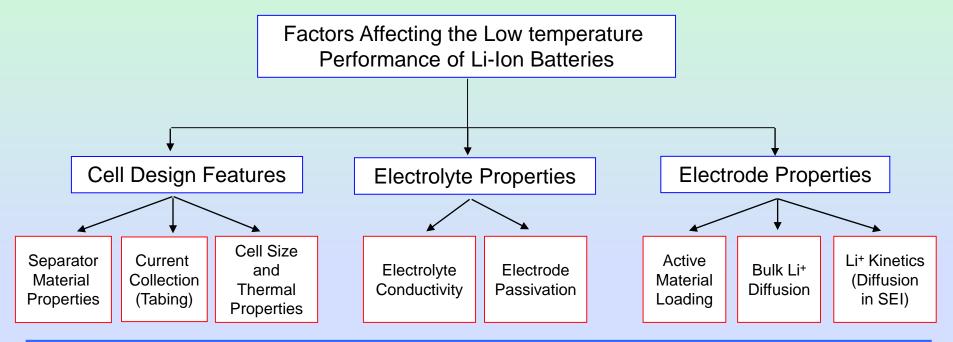


Outline

- Background
- Objectives and Approach
- Development and Demonstration of Heritage Carbonate-Based Electrolyte
 - MSP'01Mission, MER Mission, MSL Mission
- Development and Demonstration of Ester-Containing Electrolytes
 - InSight Mission
- Development of Electrolytes for Future Ocean Worlds Missions
 - Large format and small format (18650) cell approaches
 - Yardney Large Capacity Prototype Cells
 - Quallion Prototype BTE Cells
 - E-One Moli 18650-size Cells
- Conclusions



Low Temperature Lithium Ion Electrolytes Electrolyte Development: Approach/Background



- Of these factors, the electrolyte properties have the most dramatic impact on low temperature performance (i,e., if the the electrolyte is frozen the cell/battery will not operate).
- Sufficient electrolyte conductivity at low temperature is not sufficient to ensure efficient operation due to potential reactivity leading to poor kinetics and/or inadequate life aspects.
- To enable very low temperature operation (< 40°C), high diffusivity electrode materials must be identified coupled with improved cell design.

Development of Low Temperature Lithium Batteries Vision and Goal

Goal: To develop rechargeable lithium-based cells for future NASA applications which are capable of operation over a large temperature range, especially at low temperatures (-60° to +60°C).

Technology Development:

Capabilities:

- Improved Low Temperature Li-Ion Electrolyte Technology
- Gen I Electrolyte Incorporated into Demonstrated improved MSP01 and MER Batteries

Operation -20 to +40°C

- Further optimization of carbonate-based electrolytes
- capabilities of Gen II and Gen II electrolytes
- Development of improved electrolytes with aggressive solvents and salts and modified cell design.
- Will result in improved temperature range of operation



Operation - 40 to +40°C

Operation -60 to +60°C



Infusions:



2001 MSP'01 Lander **Battery** (Phoenix Battery)



2003 MER Rover **Battery**



2007 Mars Phoenix Mission



2009 Mars

Science

Laboratory



2011 Juno Mission



2018 **InSight** Lander



Mars 2020 Mission



Future Ocean Worlds Missions

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2003 Mars Exploration Rover- Rover Batteries

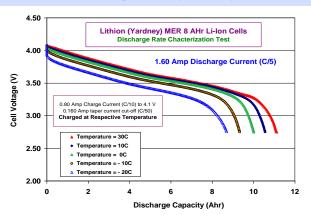


- · Lithium-ion technology was used for '03 MER Rovers
- Heritage chemistry, including electrolyte, adopted from MSP'01
- Opportunity has been operational since landing on Mars on 1/25/2004

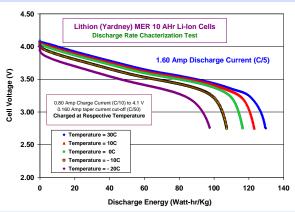
Rover Battery Requirements

- Voltage : 32-24 V
- Capacity: 16 Ah (BOL) at RT and 10 Ah at —20°C (BOL)
- Load : C/2 max at RT; Typical C/5
- Temperature : Charge at 0-25°C and discharge >-20°C
- Light weight and compact
- Long cycle life of over 300 cycles
- Long storage life of over 2 years

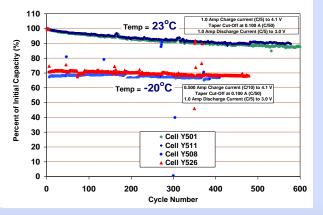
Discharge Capacity (Ah)



Discharge Energy (Wh/kg)



100% DOD Cycling Life



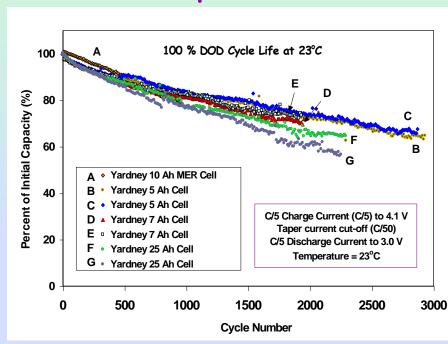
Cells contain 1.0M LiPF₆ EC+DMC+DEC (1:1:1) (Range of operation -30 to +40°C)

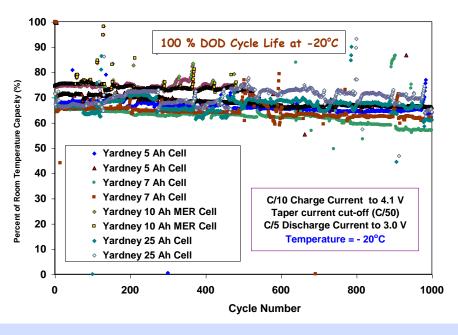
Yardney Lithium-Ion Cells for Aerospace Applications

100% DOD Cycle Life Performance

Temp = $23^{\circ}C$

Temp = $-20^{\circ}C$





- Comparable cycle life performance obtained with a range of cell sizes fabricated by Lithion, Inc. (from 5 to 25 Ahr).
 - > Stable performance displayed when continuous cycling is performed at 20°C (lower capacity fade rate compared to room temperature).

Cells contain 1.0M LiPF₆ EC+DMC+DEC (1:1:1) (Range of operation -30 to +40°C)

M. C. Smart, B. V. Ratnakumar, L. D. Whitcanack, F. J. Puglia, S. Santee, and R. Gitzendanner, "Life Verification of Large Capacity Yardney Li-ion Cells and Batteries in Support of NASA Missions", *Int. J. Energy Res*, **34**,116-134 (2010).



Mars Science Laboratory (MSL) Curiosity Rover

· Launch Date: November 26, 2011

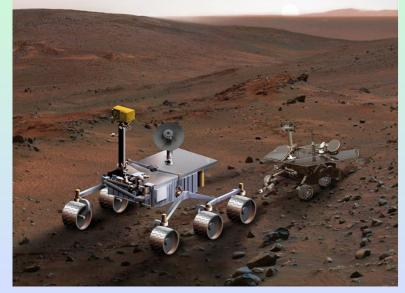
Landing Date: August 6, 2012

• Science Goals: To assess habitability: whether Mars ever was an environment able to support microbial life.

- The biggest, most advanced suite of instruments ever sent to the Martian surface.
- Analyze dozens of samples scooped from the soil and cored from rocks in the onboard laboratory to detect chemical building blocks of life (e.g., forms of carbon) on Mars.
- Landing: Parachute assisted and powered descent, lowered on tether like sky crane.
- Programmatic Goals: To demonstrate the:
 - Ability to land a very large, heavy rover to the surface of Mars (future Mars Sample Return)
 - Ability to land more precisely in a 20-kilometer (12.4-mile) landing circle
 - long-range mobility (5-20 kilometers or about 3 to 12 miles)

- Highlights:

- Curiosity has operated over 1500 Sols to-date
- After 2 years and almost 9 km of driving, Curiosity has reached the base of Mount Sharp
- During the first year, the rover fulfilled its major science goal of determining whether Mars ever offered conditions favorable for microbial life.
- As of Sol 1507, Curiosity has driven 9.16 miles (or 14.75 kilometers)



Battery Details

- Two 8-cell batteries in parallel (8s2p).
- 24-32.8 V, 86 Ah (MER, Grail, Juno Chemistry)
- Qualification Temperature range: -30° to +40°C.
- Operating Temperature Range: -20° to +30°C
- Required Life: ~ 4 years
- Surface Life: 670 Sols of operation.
- Battery temperature controlled with a combination of heaters and radiators



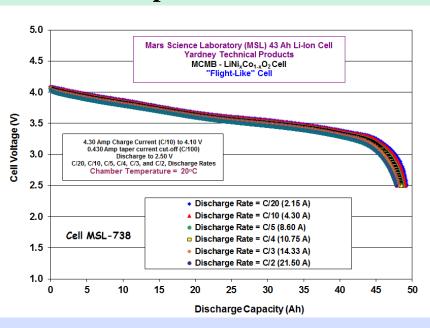
Yardney Li-ion MSL 43 Ah Li-Ion Performance Testing

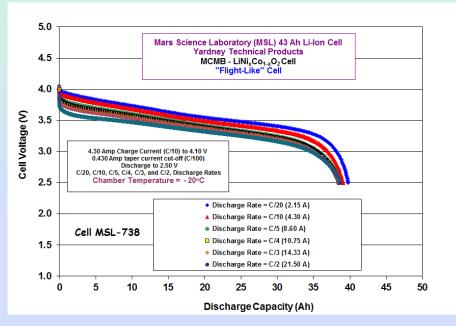
Discharge Rate Characterization Testing at 20°C and -20°C

Cell MSL-738- Discharge Capacity (Ah)

Temperature = $+20^{\circ}$ C

Temperature = -20° C





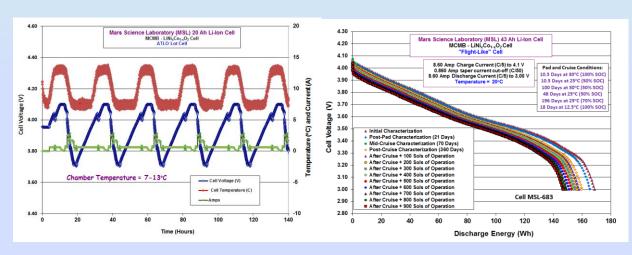
			Cell MSL- 738					Cell MSL- 757				
Temperature	Discharge Rate	Discharge Current (A)	Discharge Capacity (Ah)	Percent C/20 Capacity	Percent C/20 Capacity at 20°C	Discharge Watt-Hr (Wh)	Discharge Energy (Wh/Kg)	Discharge Capacity (Ah)	Percent C/20 Capacity	Percent C/20 Capacity at 20°C	Discharge Watt-Hr (Wh)	Discharge Energy (Wh/Kg)
20°C	C/20	2.150	49.2061	100.00	100.00	177.756	148.97	48.9692	100.00	100.00	176.858	148.02
	C/10	4.300	48.9989	99.58	99.58	176.543	147.96	48.7904	99.63	99.63	175.742	147.09
	C/5	8.600	48.6170	98.80	98.80	174.244	146.03	48.3960	98.83	98.83	173.357	145.09
	C/4	10.75	48.4333	98.43	98.43	173.141	145.11	48.2208	98.47	98.47	172.275	144.19
	C/3	14.33	48.1604	97.87	97.87	171.458	143.70	47.9510	97.92	97.92	170.588	142.78
	C/2	21.50	47.7824	97.11	97.11	168.820	141.49	47.5403	97.08	97.08	167.806	140.45

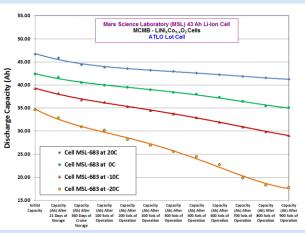
			Cell MSL- 738				Cell MSL- 757					
Temperature	Discharge Rate	Discharge Current (A)	Discharge Capacity (Ah)	Percent C/20 Capacity	Percent C/20 Capacity at 20°C	Discharge Watt-Hr (Wh)	Discharge Energy (Wh/Kg)	Discharge Capacity (Ah)	Percent C/20 Capacity	Percent C/20 Capacity at 20°C	Discharge Watt-Hr (Wh)	Discharge Energy (Wh/Kg)
- 20°C	C/20	2.150	39.7706	100.00	80.82	140.857	118.05	39.8947	100.00	81.47	141.401	118.35
	C/10	4.300	39.0600	98.21	79.38	136.220	114.16	39.2206	98.31	80.09	136.951	114.62
	C/5	8.600	38.5709	96.98	78.39	131.578	110.27	38.7713	97.18	79.17	132.541	110.93
	C/4	10.75	38.5001	96.81	78.24	130.386	109.27	38.7282	97.08	79.09	131.468	110.03
	C/3	14.33	38.4872	96.77	78.22	129.076	108.18	38.7479	97.13	79.13	130.282	109.04
	C/2	21.50	38.6546	97.19	78.56	127.644	106.98	38.9490	97.63	79.54	128.972	107.94



Performance Testing of Yardney MSL 20 Ah Li-Ion Cells Mission Simulation Testing

- After completing the cruise simulation and characterization, a number of cells were subjected to surface operation mission simulation testing. Cells were subjected to varying pad storage and cruise storage to quantify degradation.
 - ➤ The health of the cells is periodically determined throughout the life at various temperatures: +20°C, 0°C, -10°C, and -20°C.





M. C. Smart, B. V. Ratnakumar, F. C. Krause, L. D. Whitcanack, E. A. Dewell, S. F. Dawson, R. B. Shaw, S. Santee, F. J. Puglia, A. Buonanno, C. Deroy, and R. Gitzendanner, "Performance Testing of Yardney Li-ion Cells in Support of NASA's MSL and InSight Missions", NASA Aerospace Battery Workshop, Huntsville, Alabama, November 17-19, 2015.



NASA's Mars InSight Lander

- Anticipated Launch Date: May 2018
- InSight (Interior Exploration using Seismic Investigations, Geodesy and Heat Transport) is a NASA Discovery Program mission that will place a single geophysical lander on Mars to study its deep interior.
- Mission will consist of a spacecraft built by Lockheed Martin Space Systems Company based on a design that was successfully used for NASA's Phoenix Mars lander mission
- · Science Goals:
 - InSight is a terrestrial planet explorer that will address the processes that shaped the rocky planets of the inner solar system (including Earth) more than four billion years ago
 - InSight will probe beneath the surface of Mars, detecting the fingerprints of the processes of terrestrial planet formation
- In January 2016, the March 2016 launch date of InSight mission was suspended to allow the repair of a leak in a section of the prime instrument in the science payload.



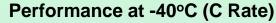
Battery Details

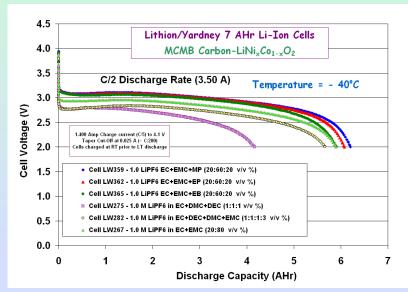
- Two 8-cell batteries (connected in parallel)
- Manufactured by Eagle-Picher Technologies / Yardney Division
- 24-32.8 V (Phoenix Battery Design)
- Qualification Temperature range: 40°C to +50°C.
- Operating Temperature Range: -30° to +35°C
- Required Life: ~ 4 years
- Surface Life: 709 Sols of operation.

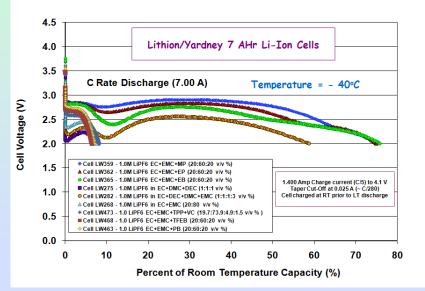
Development of Advanced Low Temperature Electrolytes

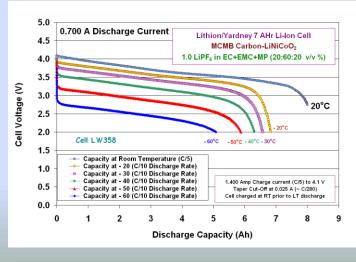
Demonstration of Ester-Based Electrolytes in Yardney Prototype Cells

Performance at -40°C (C/2 Rate)









An electrolyte formulation containing methyl propionate, 1.0M LiPF $_6$ EC+EMC+MP (20:60:20 v/v %) was demonstrated to provide improved low temperature performance over baseline all carbonate-based electrolytes (including the heritage blend), while still providing reasonable high temperature resilience.

- M.C. Smart, and B.V. Ratnakumar, L.D. Whitcanack, K.A. Smith, S. Santee, R. Gitzendanner, V. Yevoli, "Li-Ion Electrolytes Containing Ester Co-Solvents for Wide Operating Temperature Range", *ECS Trans.* **11**, (29) 99 (2008).
- M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, "Lithium-Ion Electrolytes Containing Ester Co-solvents for Improved Low Temperature Performance", *J. Electrochem. Soc.*, 157 (12), A1361-A1374 (2010).

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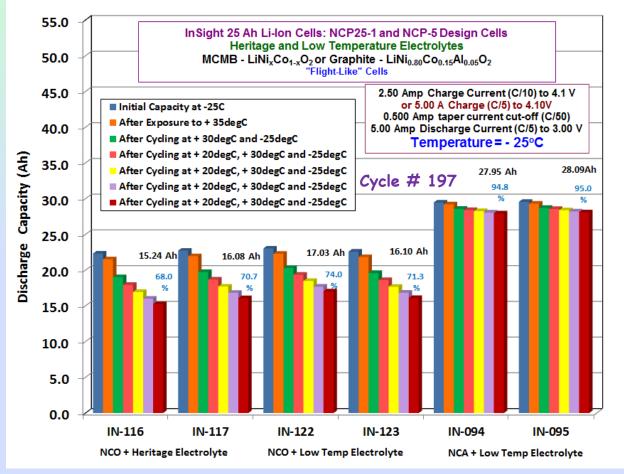
Performance Testing of Yardney NCP-25x Lithium-Ion Cells Summary of Test Plan for InSight

- Next Generation Yardney NCP-25x Li-Ion Cells
 - > 18 Cells were tested possessing four chemistry variations
 - Cells are 25 Ah nameplate capacity (based on Yardney NCP-25-1 design)
 - > Cells were subjected to rigorous performance testing to determine applicability to InSight

Cell Group (Quantity)	Cell Definition	Cathode	Anode	Material Loading	Electrolyte	
Chemistry A (5 Cells)	Heritage (Control / Phoenix Baseline)	LiNiCoO ₂ (NCO)	МСМВ	Nominal	Standard Heritage Electrolyte $1.0M \ \text{LiPF}_6 \ \text{in EC+DEC+DMC} \ (1:1:1)$	
Chemistry B (5 Cells)	Heritage, Low- Temperature Electrolyte	LiNiCoO ₂ (NCO)	МСМВ	Nominal	Low-Ester, Low-Temperature 1.0M LiPF ₆ in EC+EMC+MP (20:60:20)	
Chemistry C (5 Cells)	NextGen Chemistry, Low-Temperature Electrolyte	LiNiCoAlO ₂ (NCA)	Modified Graphite	Nominal	1.0M LiPF ₆ in EC+EMC+MP (20:60:20)	
Chemistry D (3 Cells)	NextGen Chemistry, Heritage Electrolyte	LiNiCoAlO ₂ (NCA)	Modified Graphite	Nominal	Standard Heritage Electrolyte 1.0M LiPF ₆ in EC+DEC+DMC (1:1:1)	



Performance Testing in Support of InSight Summary of Results: Group 1 Cells (Discharge Capacity at -25°C)



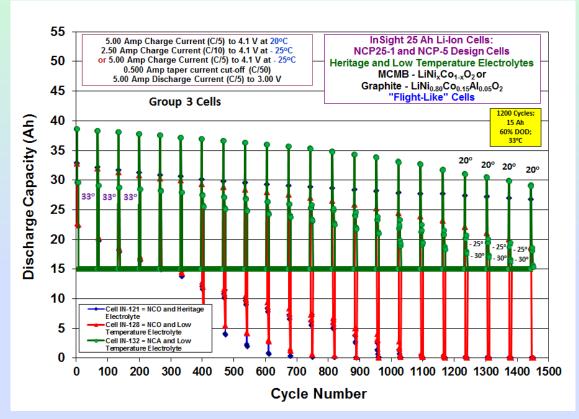
The NCA+ Low Temperature Electrolyte chemistry delivers improved capacity at -25°C compared with the NCO heritage (> 78% improvement) and displays dramatically better low temperature capacity retention throughout the life of the cells.

M. C. Smart, S. F. Dawson, R. B. Shaw, L. D. Whitcanack, A. Buonanno, C. Deroy, and R. Gitzendanner, "Performance Validation of Yardney Low Temperature NCA-Based Li-ion Cells for the NASA Mars InSight Mission", NASA Aerospace Battery Workshop, Huntsville, Alabama, November 18-20, 2014.



Performance Testing in Support of InSight

Summary of Results: Group 3 (Discharge Capacity, Ah)

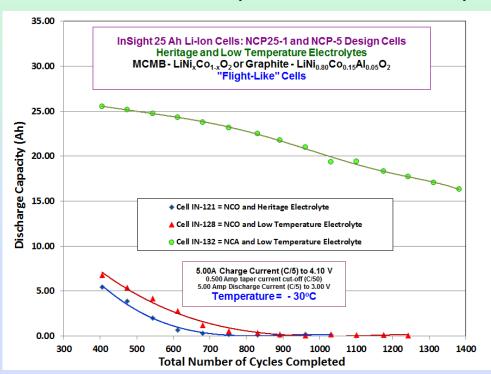


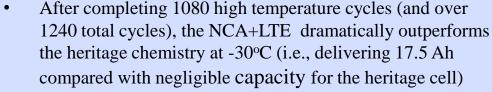
- The Group 3 cells were cycled at high temperature $+33^{\circ}C$ and periodically characterized at $+20^{\circ}$, -25° , and $-30^{\circ}C$
- The NCA+LTE cell IN-132 delivered 18.79 Ah at -25°C (cycle 1,378) and 16.31 Ah at -30°C (cycle 1,382) In contrast, the NCO+Heritage only delivered 0.100 Ah and the NCO+LTE delivered 0.084Ah at -25°C (cycle 1,378)
- Cells cycled under flight-like conditions (i.e., C/5 charge rate to 4.10V)
- Cells have completed 1,200 accelerated cycles at high temperature (i.e., 33°C)

M. C. Smart, B. V. Ratnakumar, F. C. Krause, L. D. Whitcanack, E. A. Dewell, S. F. Dawson, R. B. Shaw, S. Santee, F. J. Puglia, A. Buonanno, C. Deroy, and R. Gitzendanner, "Performance Testing of Yardney Li-ion Cells in Support of NASA's MSL and InSight Missions", NASA Aerospace Battery Workshop, Huntsville, Alabama, November 17-19, 2015.

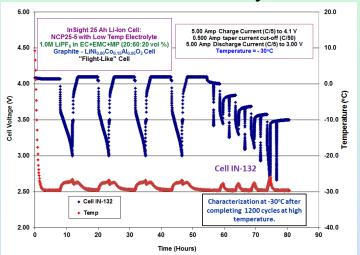
Performance Testing in Support of InSight

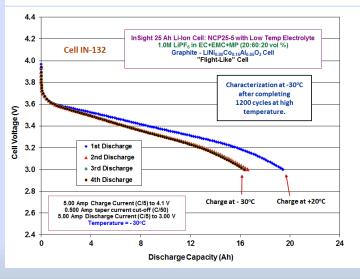
Summary of Results: Group 3 (Performance at -30°C)





• No evidence of Li plating was observed with the cells using a C/5 charge rate (5.0A) at -30°C.

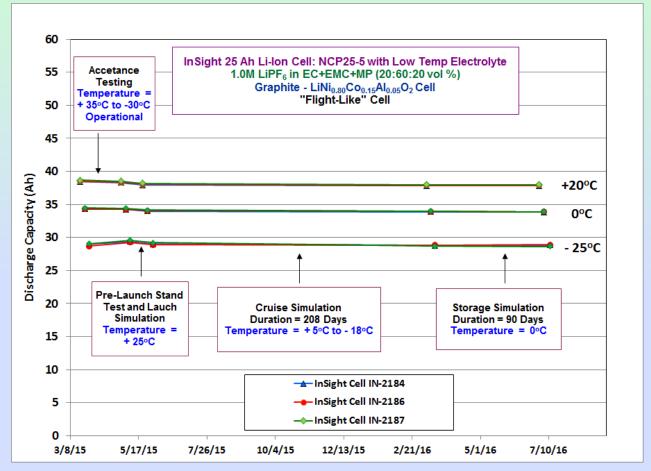




M. C. Smart, B. V. Ratnakumar, F. C. Krause, L. D. Whitcanack, E. A. Dewell, S. F. Dawson, R. B. Shaw, S. Santee, F. J. Puglia, A. Buonanno, C. Deroy, and R. Gitzendanner, "Performance Testing of Yardney Li-ion Cells in Support of NASA's MSL and InSight Missions", NASA Aerospace Battery Workshop, Huntsville, Alabama, November 17-19, 2015.

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Performance Testing of InSight Yardney Li-Ion Cells Status of Group 5 Cell Testing



- Less than 1.5 % capacity loss was observed at all three temperatures after being subjected to acceptance testing, long term cruise simulation, and 3 months of post-cruise storage.
- Due to the postponement of the InSight mission, we are currently simulating the long term storage of the cells in addition to the planned mission simulation testing.



Background: Mission Concept Needs Potential Future Ocean Worlds Power System Needs

Power: ~ 100 W

Voltage ~ 28 V

Operational Life on Surface: 7-14 days

(2 - 4 Europa days)

Mission Survivability/Shelf Life: 15 years

Operating Temperature: - 60°C to 40°C

Radiation Tolerance: > 2-4 Mrad

Planetary Protection: Required

- A potential future mission to Europa, or other Ocean World, could benefit significantly from a low temperature rechargeable battery with full operational capability when coupled with solar arrays, enabling a means to meet a 14 day requirement:
 - If RHU's or RTG's were not selected to provide heat, low temperature batteries would be desired
 - Improved low temperature performance (down to -60°C) would reduce thermal power loads
 - Results in lower power sub-system and thermal power sub-system mass
 - Extended mission durations are possible (> 14 days)

Pre-Decisional Information -- For Planning and Discussion Purposes Only

EUROPA

Background: Technology Development Targets

- Combined rechargeable Li-ion batteries/solar arrays could augment primary batteries for extended missions:
 - Current technology limited to operation at temperatures above -30°C.
 - One of the key challenges is *charging* at low temperatures, due to reduced charge acceptance.
 - Low temp charging and Li plating can lead to increased rate of cell degradation and premature cell failure.
 - Improved low temperature performance (-40 to -60°C) will reduce required thermal management power and complexity, by bringing operational temperature limits in-line with primary batteries and avionics.

Performance Metrics	State-of-practice Rechargeable Batteries	Proposed Rechargeable Low Temperature Li-lon Batteries	Proposed Rechargeable Low Temperature Li-lon Batteries (stretch goal)	
Cell Specific Energy at +20°C (Wh/kg)	130-150	150-200	150-200	
BOL Cell Specific Energy at Low Temperature (Wh/kg, discharge)	95-115 at -20°C	≥100 at -40°C	75-100 at -60°C	
Cycle Life	>500	300	300	
Lower Temperature Charging Limit (°C)	-20 to -30	-40	-60	
Operational Temperature (°C)	-30 to +35	-40 to +35	-60 to +35	
Shelf Life (Years)	15	15	15	
Heritage	Phoenix, InSight Li-ion			

Primary goal is to demonstrate > 100 Wh/kg at -40°C (with both charging and discharging).



Objective

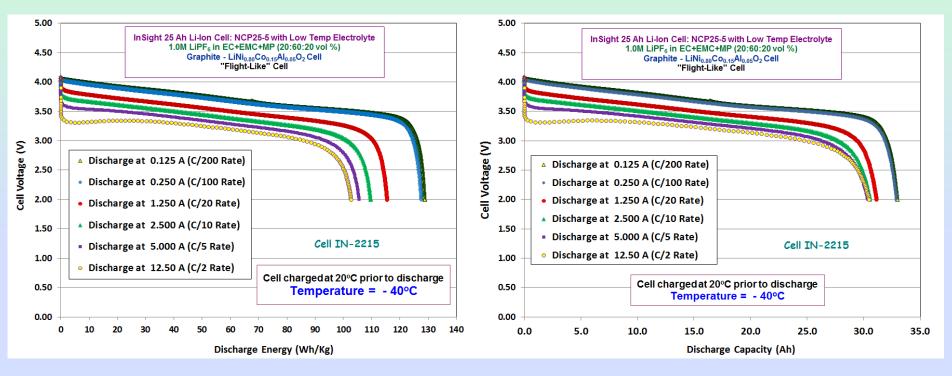
- Develop rechargeable Li-Ion batteries that can operate at low temperatures for potential missions to Icy Moons
- Improve the specific energy of Li-ion batteries at low temperatures (increase the Wh/kg available)
- > Extend the low temperature operating temp range (to -40°C or -60°C)
- > Demonstrate continuous operation at low temperature

Approach

- Benchmark state of practice (SOP) aerospace quality Li-ion cells at low temperatures.
- Further develop JPL low temperature electrolytes to support charging and discharging down to low temperatures (- 40°C).
- Work with vendors to infuse electrolytes into flight qualifiable-cell designs optimized for low temperature operations.
- Demonstrate improved low temperature performance in prototype Li-ion cells.
- Utilize experimental three-electrode cells to elucidate the aspects of low temperature operation, including determining the kinetics as a function of temperature.



Performance Testing of InSight Yardney NCP-25-6 Cells Evaluation of Low Temperature Performance for Future Potential NASA Missions to Icy Moons



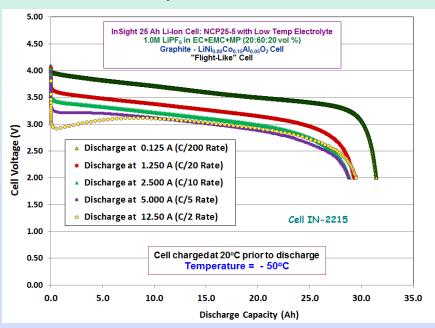
- > The next generation InSight chemistry containing the MP-based low temperature electrolytes delivers good rate capability at -40°C, delivering over 102 Wh/kg at a C/2 rate (or 12.50A).
- > Demonstrates that technology is well suited to support high power transmission events.

M. C. Smart. et al., "The Use of Low Temperature Electrolytes in High Specific Energy Li-Ion Cells for Future NASA Missions to Icy Moons", 229th Meeting of the Electrochemical Society, San Diego, California, June 1, 2016.

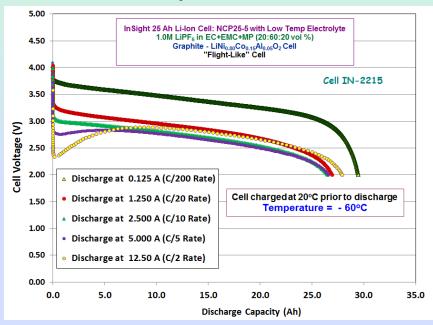


Performance Testing of InSight Yardney NCP-25-6 Cells Evaluation of Low Temperature Performance for Future Potential NASA Missions to Icy Moons

Temperature = - 50°C



Temperature = - 60°C



- > The next generation InSight chemistry containing the MP-based low temperature electrolytes delivers good rate capability at -50°C, delivering over 90 Wh/kg at a C/2 rate (or 12.50A).
- > Good performance also demonstrated at -60°C

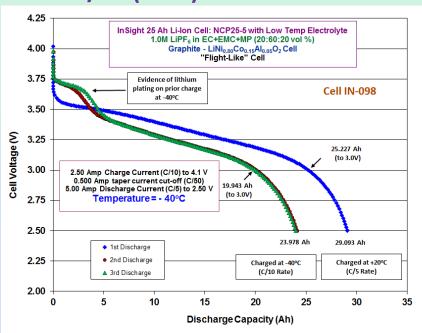


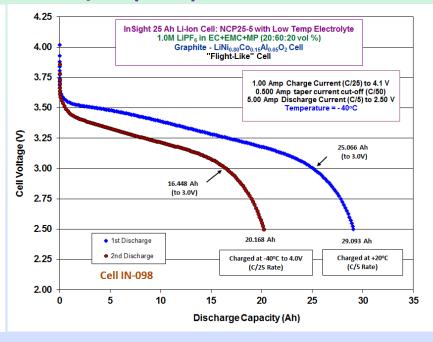
Performance Testing in Support of InSight Project

Charging and discharging at-40°C

C/10 (2.5A) to 4.10V at -40°C

C/25 (1.0A) to 4.00V at -40°C



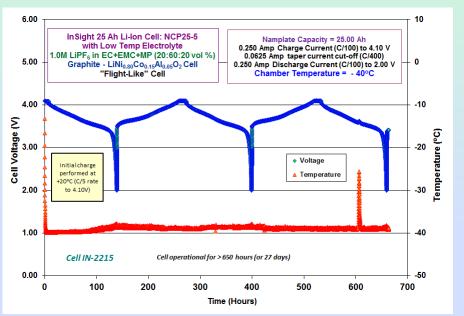


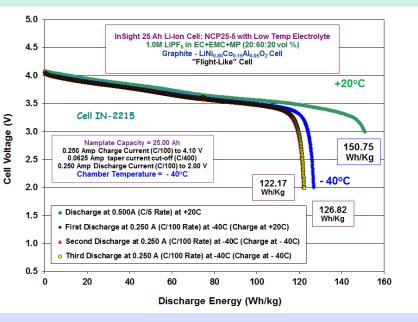
- ► When NCA/LTE cells were cycled at -40°C using C/10 charge rate, Li plating was observed on the anode
- This is indirectly observed by the higher voltage plateau on the subsequent discharge (i.e., the lower overpotential of lithium stripping compared to Li+ de-intercalation from graphite).
- ➤ Results led to the evaluation of lower charge rates and charge voltage test at -40°C (i.e., C/25 charge rate to 4.00V), where no evidence was observed.
- Subsequent testing established only modest plating at -35°C (C/5 rates to 4.10V) and no plating evident at -30°C (using C/5 charge rates to 4.10V)

Performance of InSight 36 Ah (Yardney NCP-25-1 Design) Li-Ion Cells:

(Next Generation NCA Chemistry + Low Temperature Electrolyte)

Cycling Continuously at -40°C at C/100 Rates (both Charging and Discharging)





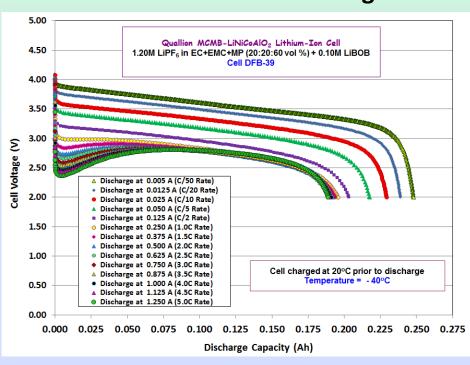
- ➤ The next generation InSight chemistry containing the MP-based low temperature electrolytes delivers good reversibility when cycled continuously at -40°C using low rates (i.e., delivering ~ 122 Wh/kg at -40°C).
- > No evidence of lithium plating observed when cycled under these conditions.
 - Performance demonstration exceeds target of 100 Wh/kg at -40°C.

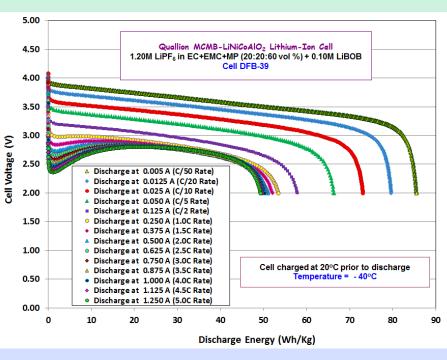


Performance of Quallion BTE Custom Cells

(Cells obtained under DOE program and NASA SBIR program)

Discharge Rate Capability at -40°C

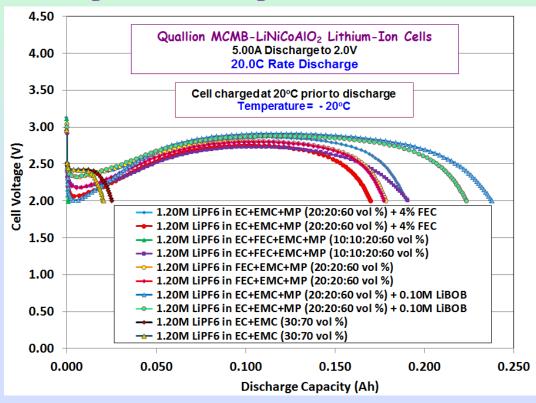




- > Quallion cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support high power discharge. Excellent retention of room temperature performance.
- > Electrolyte selection of new generation of cells based on results of initial assessment.
 - Larger cell designs provided by Quallion (up to 15 Ah) will result in higher specific energy at low temperatures compared to the small BTE cells (0.25 Ah).

Performance of Methyl Propionate-Based Electrolytes in Prototype Cells Discharge Performance at - 20°C

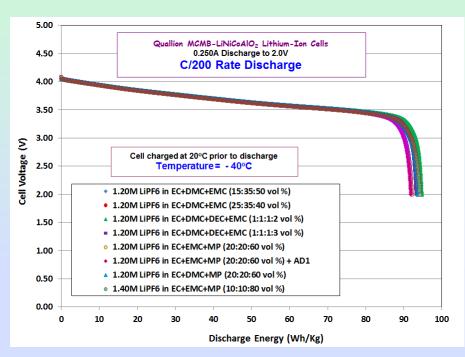
High Rate Discharge Performance at Low Temperature (20C Rates)

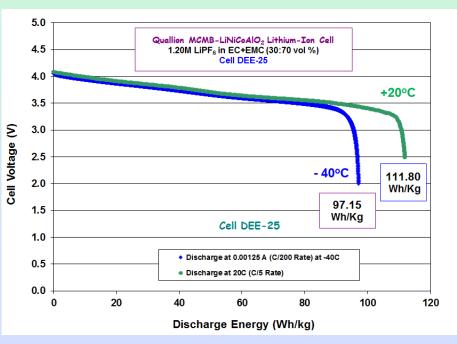


- Demonstration of high power capability of methyl propionate-based electrolytes in Quallion 0.25 Ah Li-ion cells.
 - A number of MP-based electrolytes have been further developed that contain FEC and LiBOB as additives.
- Cells observed to support 20C discharge rates at -20°C.
- The cell containing the electrolyte with methyl propionate and LiBOB has displayed very high power capability at -20°C, being able to provide over 60 Wh/kg at a 20C discharge rate.
 - All of the MP-based electrolytes displayed dramatically improved power capability.
- At a 20C discharge rate at -20°C, the cell containing the MP-based electrolyte delivered over 11 times greater discharge energy (i.e., 62.2 Wh/kg compared to only 5.5 Wh/kg for the baseline).
 - However, how do these systems behave when required to be charged at -40°C or lower ??



Performance of Quallion BTE Custom Li-Ion Cells C/200 Discharge Rate at -40°C

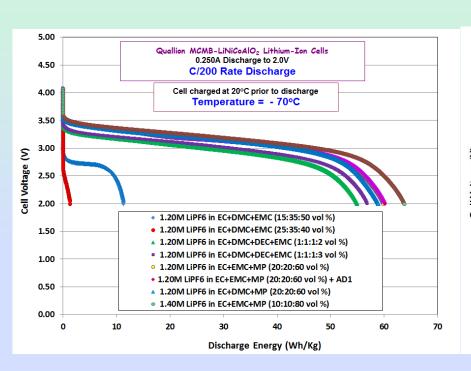


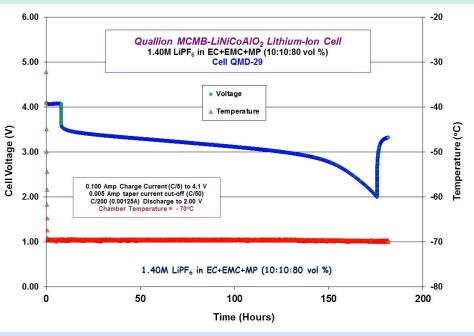


- Quallion cells have been demonstrated to provide consistent low temperature performance at -40°C at low rate, with the little impact of electrolyte type when charge at room temperature.
- Excellent retention of room temperature performance is observed.
 - Larger cell designs provided by Quallion (up to 15 Ah) will result in higher specific energy at low temperatures compared to the small BTE cells (0.25 Ah).



Performance of Quallion BTE Custom Cells C/200 Discharge Rate at -70°C





- > Quallion cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support discharge at -70°C (with over 165 hours of operation).
- > Electrolyte selection of new generation of cells based on results of initial assessment.
 - Larger cell designs provided by Quallion (up to 15 Ah) will result in higher specific energy at low temperatures compared to the small BTE cells (0.25 Ah).

Performance Testing of Quallion Cells in Support of PUFFER:

- Assess viability of using Quallion BTE Li-Ion cells for the Pop Up Flat Folding Explorer Robot (PUFFER) program.
- Evaluate the performance capability of Quallion BTE Li-Ion cells to operate at very low temperatures (-40°C to -70°C).
- Determine the capabilities of the Quallion BTE Li-ion cells to meet preliminary concept mission requirements.

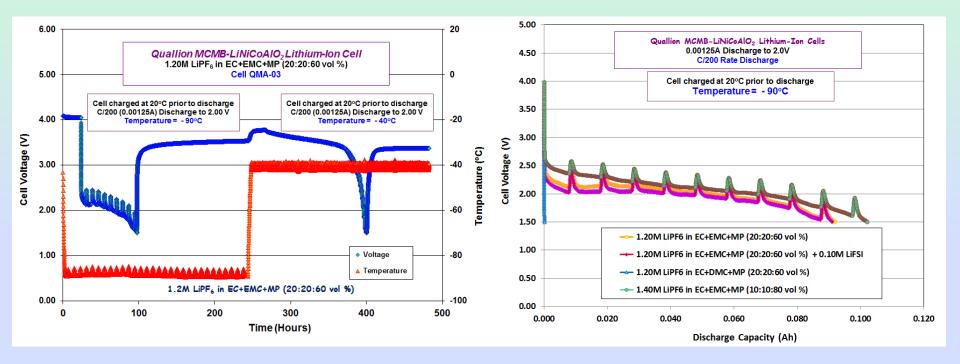
Preliminary Configuration and Tentative Requirements:

- Configuration: Two Li-ion cells connected in series
 - Currently baselining two Quallion QL0370B Li-Ion Cells
- Operating Temperature Range:
 - Maximum temperature = + 20°C
 - Minimum charge temperature = 40°C
 - Minimum discharge temperature = 70°C
 - Minimum survival temperature = 120°C
- Energy and Power Requirements:
 - Nominal discharge current = 300 mA
 - Peak discharge current = 1500 mA
 - Nominal charge current = 55 mA
 - Peak charge current = 180 mA
 - Total discharge energy required per sol = 1 Wh
- Lifetime Requirements:
 - Operational lifetime on surface = > 10 sols
 - Operational time per sol = 1.33 hours per sol





Performance of Quallion BTE Cells at Low Temperature: Low Temperature Survivability Test at -90°C



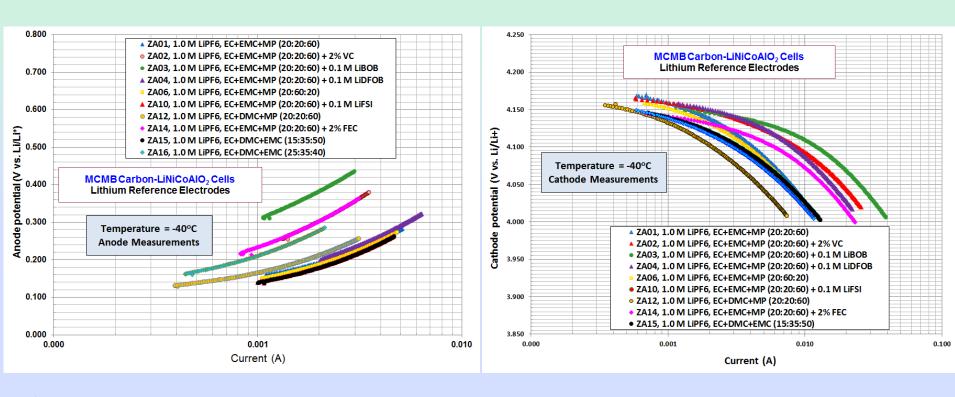
- > Quallion cells have been demonstrated to provide excellent low temperature survivability characteristics, being capable of supporting operation at -90°C and long term dwell periods.
 - Cells soaked at -90°C for 24 hours prior to discharge
 - Cells discharged at C/200 rate at -90°C to 1.50V
 - Cells allowed to dwell at -90°C for > 5 days prior to warming to -40°C
 - Cells discharged at C/200 rate at -40°C to 1.50V
 - Cumulative capacity of discharge determined (-90°C + -40°C)
 - Capacity determined to be comparable with prior C/200 discharge testing at -40°C



Performance of Quallion Experimental 3-Electrode Cells

(Electrodes obtained from Quallion)

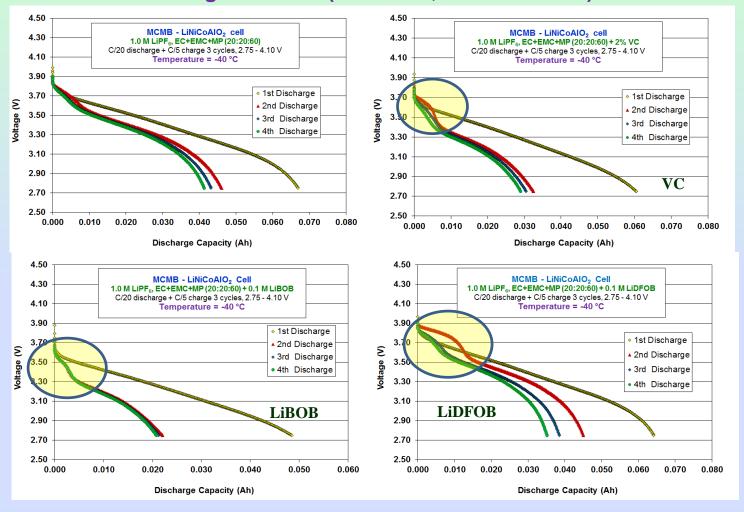
Tafel Polarization Measurements at - 40°C



- ➤ Experimental 3-electrode cells with Quallion electrodes display reasonable robustness to charging at -40°C when low rates are employed.
- ➤ We are currently evaluating a number of electrolytes in these 3-electrode cells, and attempting to correlate the relative kinetics with the propensity of lithium plating.

Charge Behavior of MCMB/LiNiCoAlO₂ Cells at Low Temperature

Charge at - 40°C (C/5 Rates, 2.75V to 4.10V)



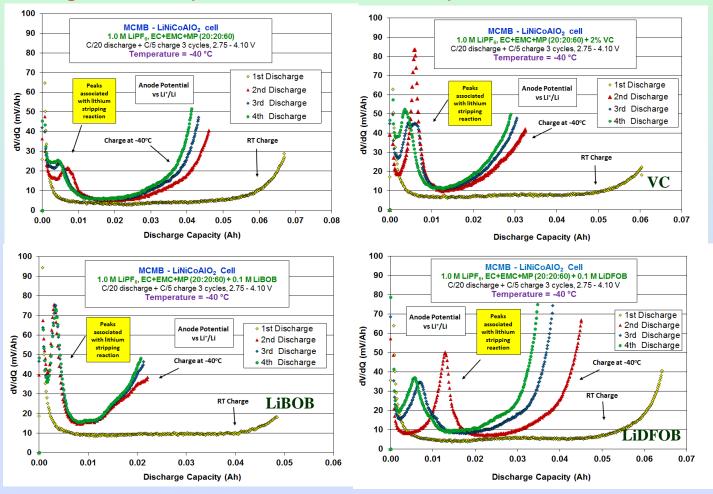
▶ In experimental three electrode cells containing Quallion electrodes, all additives appear to lead to increased lithium plating compared to the baseline solution at -40°C using C/5 charge rates.

M. C. Smart. et al., 227th Meeting of the Electrochemical Society, Chicago, Illinois, May 25-29, 2015 (Abstract #47562).

Charge Behavior of MCMB/LiNiCoAlO₂ Cells at Low Temperature



Charge at - 40°C (C/5 Rates, 2.75V to 4.10V) - Quallion Electrodes



- Differential voltage/capacity plots of the anode potential during cycling is insightful in determining which sample experiences the greatest amount of lithium plating/stripping.
- ▶ When the discharges at -40°C are analyzed all of the cells with additives result in notable stripping peaks.
 - M. C. Smart. et al., 227th Meeting of the Electrochemical Society, Chicago, Illinois, May 25-29, 2015 (Abstract #47562).



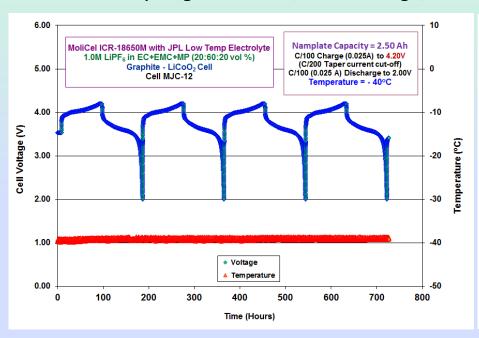
Performance of E-One Molicel ICR-18650 M Custom Cells

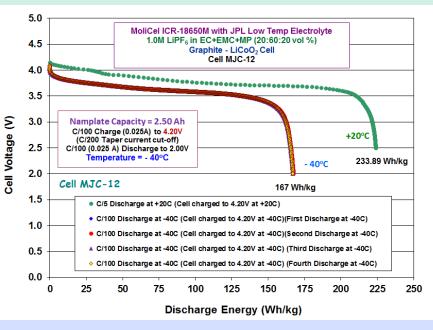
Charge and Discharge at -40°C (C/100 Rates))(Charge Voltage = 4.20V)

JPL Electrolyte "C" = 1.0M LiPF₆ in EC+EMC+MP (20:60:20 vol %) [InSight Electrolyte]

Continuous cycling at -40°C (4.20V Charge)

Specific Energy (Wh/kg) at -40°C





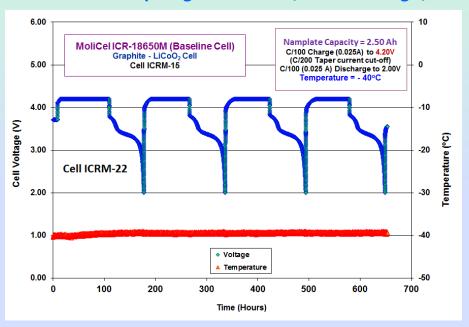
- ► Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., 167 Wh/kg).
- ➤ No lithium plating observed when charging to 4.20V at -40°C using low rate charge.
- The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number custom JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).



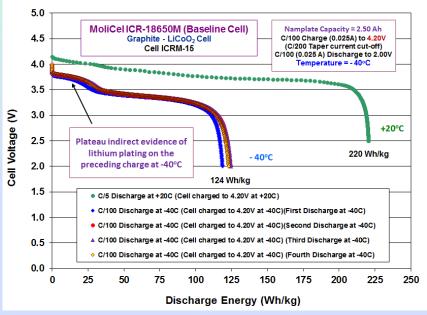
Performance of E-One Molicel ICR-18650 M Cells Charge and Discharge at -40°C (C/100 Rates))(Charge Voltage = 4.20V)

Baseline Commercial Off-the-Shelf Cell (COTS)

Continuous cycling at -40°C (4.20V Charge)



Specific Energy (Wh/kg) at -40°C

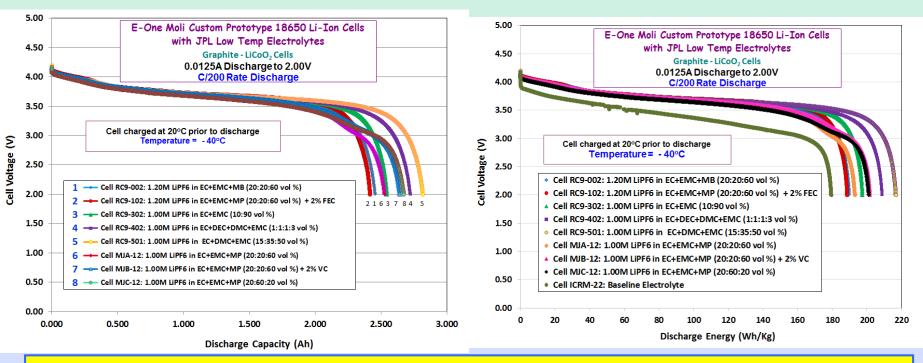


- ➤ Although good specific energy at -40°C is observed with the baseline commercial cell when charging to 4.20V at -40 (C/100) (i.e., > 124Wh/kg), there is evidence of lithium plating which leads to cell degradation.
 - The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).

Performance of E-One Moli Custom Prototype 18650 Cells at Room Temperature: Characteristization at - 40°C (C/200 Discharge to 2.0V)

Discharge Capacity (Ah)

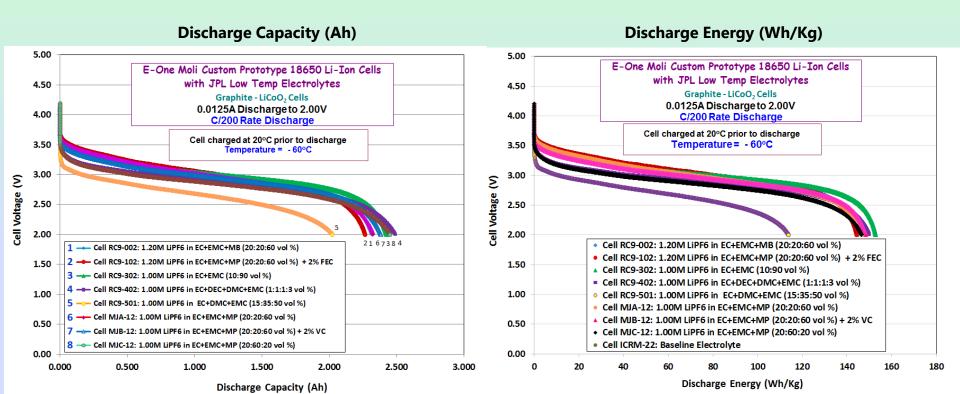
Discharge Energy (Wh/Kg)



- ➤ With charging at room temperature, excellent specific energy can be observed at low rate (C/200) at -40°C.
- Over 200 Wh/kg was observed for many electrolyte variations.
- At these low rates, the all carbonate-based electrolyte systems provided the highest specific energy.

M. C. Smart, F. C. Krause, J. –P. Jones, L. D. Whitcanack, B. V. Ratnakumar, E. J. Brandon, and M. Shoesmith, "Low Temperature Electrolytes in High Specific Energy 18650 Li-Ion Cells for Future NASA Missions", 2016 Prime Pacific Rim Meeting on Electrochemical and Solid-State Science, Honolulu, HI, October 2-7, 2016.

Performance of E-One Moli Custom Prototype 18650 Cells at Room Temperature: Characteristization at - 60°C (C/200 Discharge to 2.0V)



- With charging at room temperature, excellent specific energy can be observed at low rate (C/200) at -60°C.
- Over 150 Wh/kg was observed for many electrolyte variations.

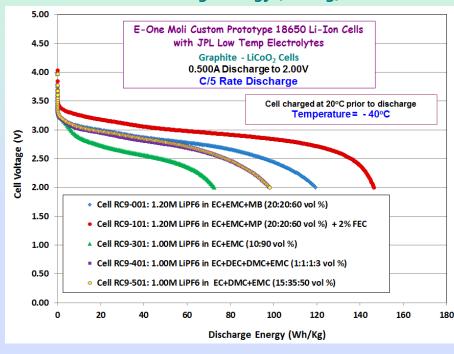
M. C. Smart, F. C. Krause, J. –P. Jones, L. D. Whitcanack, B. V. Ratnakumar, E. J. Brandon, and M. Shoesmith, "Low Temperature Electrolytes in High Specific Energy 18650 Li-Ion Cells for Future NASA Missions", 2016 Prime Pacific Rim Meeting on Electrochemical and Solid-State Science, Honolulu, HI, October 2-7, 2016.

Performance of E-One Moli Custom Prototype 18650 Cells at Low Temperature: Discharge Characteristics at -40°C (Room Temperature Charge) C/5 Discharge to 2.00V

Discharge Capacity (Ah)

5.00 E-One Moli Custom Prototype 18650 Li-Ion Cells 4.50 with JPL Low Temp Electrolytes Graphite - LiCoO2 Cells 0.500A Discharge to 2.00V 4.00 C/5 Rate Discharge 3.50 Cell charged at 20°C prior to discharge Temperature = -40°C Cell Voltage (V) 3.00 2.50 2.00 Cell RC9-001: 1.20M LiPF6 in EC+EMC+MB (20:20:60 vol %) 1.50 Cell RC9-101: 1.20M LiPF6 in EC+EMC+MP (20:20:60 vol %) + 2% FEC 1.00 ▲ Cell RC9-301: 1.00M LiPF6 in EC+EMC (10:90 vol %) Cell RC9-401: 1.00M LiPF6 in EC+DEC+DMC+EMC (1:1:1:3 vol %) 0.50 Cell RC9-501: 1.00M LiPF6 in EC+DMC+EMC (15:35:50 vol %) 0.00 0.000 0.500 1.000 1.500 2.000 2.500 3.000 Discharge Capacity (Ah)

Discharge Energy (Wh/Kg)



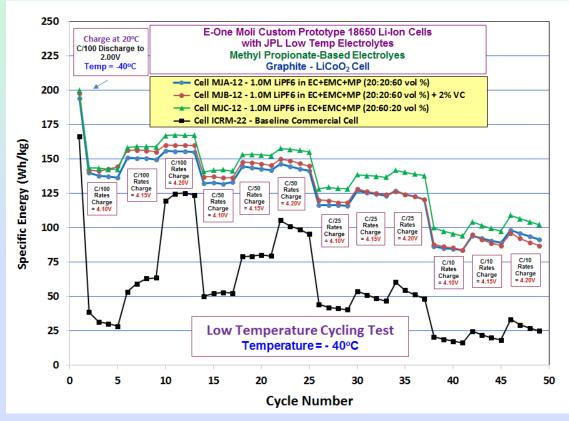
- Excellent specific energy at -40°C observed using a moderate rate discharge (C/5) with MP-based electrolyte (i.e., > 145 Wh/kg). Use of all carbonate-based electrolytes also lead to excellent discharge performance at low temperature (i.e., > 95 Wh/kg).
- Rate capability of cells with ester-based electrolytes at low temperatures is far superior to cells that contain the all carbonate-based electrolytes.

M. C. Smart, F. C. Krause, J. –P. Jones, L. D. Whitcanack, B. V. Ratnakumar, E. J. Brandon, and M. Shoesmith, "Low Temperature Electrolytes in High Specific Energy 18650 Li-Ion Cells for Future NASA Missions", 2016 Prime Pacific Rim Meeting on Electrochemical and Solid-State Science, Honolulu, HI, October 2-7, 2016.



Performance of E-One Moli Custom Prototype 18650 Cells

Continuous cycling at -40°C: Effect of charge voltage and charge rate

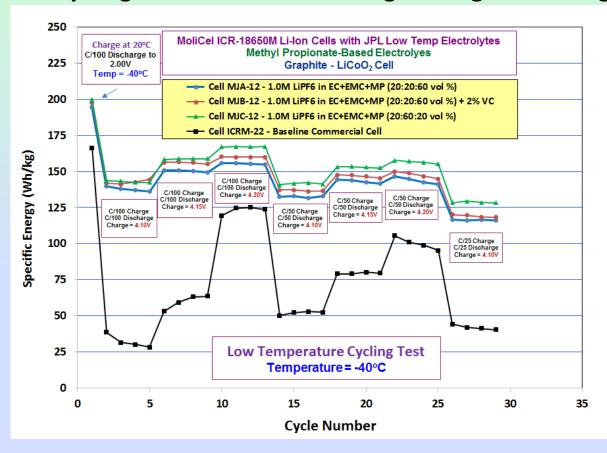


- > Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 167 Wh/kg).
- > At higher charge rates and charge voltage, there may be some lithium plating occurring, which may account for the higher capacity fade observed.
- The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).



Performance of E-One Molicel ICR-18650 M Custom Cells

Continuous cycling at -40°C: Effect of charge voltage and charge rate



- > Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., > 167 Wh/kg).
- Cells have been continuously cycled at -40°C since 10/22/2015 (over 5.5 months of operation)
- The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).



Summary and Conclusions:

- ➤ The SOP heritage all carbonate chemistry has been demonstrated to display good low temperature performance and life over a temperature range of -20°C to +40°C.
 - Electrolyte used on MER, Phoenix, Juno, Grail, and MER
- Due to the need for good low temperature capability throughout the mission, and the favorable results obtained with this testing program, the InSight project has adopted the NCA+LTE chemistry for the flight battery.
- Beginning of life (BOL), the NCA-based cells delivered >15% improvement in the capacity and energy delivered at ambient temperature and 31% more capacity at -25oC compared to the NCO-based chemistries.
- The SOA aerospace Li-ion InSight chemistry containing a JPL developed MP-based low temperature electrolytes delivers good reversibility when cycled continuously at -40°C using low rates (i.e., delivering ~ 122 Wh/kg at -40°C).
- Quallion BTE cells have been demonstrated to provide excellent low temperature characteristics, with the ability to support high power discharge.
- Quallion cells have been demonstrated to provide excellent low temperature survivability characteristics, being capable of supporting operation at -90°C and long term dwell periods.
- ➤ The custom Moli ICR-M cells with JPL electrolytes display improved cycling performance at -40°C compared to the baseline. A number of cells containing JPL electrolytes have been demonstrated to meet programmatic target of >100 Wh/kg (both charge and discharge at -40°C).
 - Excellent specific energy at -40°C observed using a low rate charge and discharge (C/100) (i.e., 167 Wh/kg) when charging to 4.20V
 - No lithium plating observed when charging to 4.20V at -40°C using low rate charge.



Acknowledgments

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